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Advanced characterization of rare earth element minerals in coal utilization byproducts using multimodal image analysis

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ABSTRACT

Multimodal microanalytical characterization techniques are applied to identify and quantify rare earth element (REE) and REE + Y (REY) bearing mineral phases in coal utilization byproducts (CUB) from various coal-fired power plants. The characterization work provides quantitative assessments of REE in coal and CUB as obtained from 2- and 3D imaging, elemental mapping, volumetric estimates, and advanced high-resolution pixel classification. REY-bearing phosphate minerals rhabdophane (Ce,La)(PO_4·H_2O), monazite (Ce,La,Nd,Th)(PO_4,SiO_4), xenotime (YPO_4,SiO_4), and apatite ($Ca_5(PO_4)_3$(F,Cl,OH), as well as REE-enriched calcium oxide were identified via electron microscopy and microprobe analysis. The minerals generally occurred as 1–20 μm-long crystals in the rock and ash samples. The most notable finding was that REEs are present as monomineralic grains dispersed within the ash, as well as fused to or encapsulated by amorphous aluminosilicate glass particles, also referred to as slag. It is indicative that conventional coal combustion processes sequester REE-bearing mineral phases such as rhabdophane, monazite, and zircon from the coal feed into aluminosilicate glass phases. The advanced microscopy and image analysis techniques applied in this study make it possible to deduce the average density of ash particles and quantify REE phases encapsulated in glass. Consequently, these REE phases may be targeted and recovered via density separation. These findings advance resource recovery techniques and commercial REE separation technologies for coal and combustion byproducts.

1. Introduction

Since 1985, the United States has consumed > 800 million tons of coal per year with nearly 90% used for electricity generation (US-EIA Energy Review, 2016). Coal-fired electric utilities produce over 100 million tons of coal utilization byproducts (CUB) annually (ACA, 2014). The U.S. Department of Energy (DOE) defines CUB as fly ash, bottom ash, boiler slag, fluidized-bed combustion ash, or flue gas desulphurization materials produced from the combustion of coal or the cleaning of stack gases (US-DOE Topical Report 24). Industrial and engineering uses for CUB solid residues have reduced fly ash waste. However, nearly 75 million tons of CUB are disposed of in landfills or storage ponds annually (ACA, 2014). Given the reliance on imported REYs, there is a need to identify a viable domestic source of critical elements (e.g., REY, Li, Co, Sc, and Ga) in order to increase domestic production for several sectors of the U.S. economy (e.g. catalysts, electronics, magnets, batteries, and other applications related to national security and energy independence).

Rare earth elements (REEs or lanthanides) and REE + yttrium (REY) concentrations are reported for coal beds and coal fly ash from around the world (Dai et al., 2017a; Dai et al., 2016; Franus et al., 2015; Hower et al., 1999, 2013; Rozelle et al., 2016; Seredin, 1996; Schatzel and Stewart, 2003; Warwick et al., 1997). Seredin and Dai (2012) comprehensively reviewed coal deposits and coal ash as an alternative source of REY and showed that REY is enriched in coal seams as well as the overlying and underlying strata. Enrichment of REY in coal is typically equal to or exceeds estimates of REY concentrations in conventional REY ore deposits (Dai and Finkelman, 2018; Seredin and Dai, 2012).

The physical and chemical composition of CUB produced by power plants is based on a combination of geologic history, industrial preparation methods, and specific combustion processes (Brownfield et al., 2005; Taggart et al., 2016). High-rank (e.g., bituminous and anthracite) coal and coal ash tend to have the highest REE content, as the enrichment of REE in coal varies greatly and depends on geological conditions (Ketris and Yudovich, 2009; Rudnick and Gao, 2012). Rare earth element concentrations for > 700 CUB and coal preparation samples, including fly ash, bottom ash, feed coal, reject coal, and underclay, are

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Table 1
Sample descriptions and attributes.

ID	Description
251	Ponded and landfill fly ash collected from an ash disposal site at a power plant in Kentucky, USA. Feed coal from central Appalachian basin coal region.
339	Ash pond sample containing mostly fly ash with a lesser amount of bottom ash. Collected from a pulverized coal power plant in Ohio, USA. Coal seam(s) unidentified.
345	Dry fly ash collected from a pulverized coal power plant in Ohio, USA. Coal seam(s) unidentified.
357	Dry ash pond sample containing mostly bottom ash with lesser amount of fly ash. Collected from a pulverized coal power plant in Ohio, USA. Coal seam(s) unidentified.
443	Pit Flint Clay Roof Rock. As-received sample composed of a fine powder (clay-sized) grain fraction and larger, angular rock fragments (1–20 mm long).
508	Heavy Media Cyclone (HMC) coal preparation plant reject. As-received sample composed of a fine powder fraction and larger, rounded rock fragments (1–10 mm long) relatively homogenous in size.

reported on the National Energy Technology Laboratory (NETL) Research and Innovation Center database housed on the Energy Data Exchange website (www.edx.netl.gov). Higher than average concentrations of rare earths in CUB, along with the abundance of CUB available for extraction, make coal and associated combustion byproducts a viable target for REE resource recovery.

Analysis of the United States Geological Survey Coal Quality Database reveals that domestic coal seams are a significant potential resource for REY as well as non-REY critical elements such as Li, Sc, Co, and Ga (Ekmann, 2012; Lin et al., 2018; Luttrell et al., 2016). Rozelle et al. (2016) expanded the coal-associated resource potential by showing that U.S. coal production byproducts are a source of REE. Rare earth element trends in CUB are predominantly based on the origin of feed coal (Kutchko and Kim, 2006). A study of major coal feedstocks in the United States ranked the REE content of coal from different geographic locations (Taggart et al., 2016). Taggart et al. (2016) characterize U.S. fly ashes of different geologic origin and show an average total REE content in Appalachian coal combusted ashes of ~591 ppm, greater than the Illinois and Powder River Basin coals at 403 and 337 ppm, respectively. The concentration of major elements (Al, Si, and Fe) in ash particles vary among coal sources. The most notable difference lies in the percentages of SiO_2, Al_2O_3, and Fe_2O_3 in the ash, with the major elemental signatures for three coal regions as follows: Appalachian (high Si and Al, low Ca), Illinois Basin (high Fe, low Ca), and Powder River Basin (low Si and Al, high Ca). The high total REE and ratio of heavy elements (Ho, Er, Tm, Lu, and Yb) to light elements (La, Ce, Nd, and Sm) in low-ash samples indicates REE may preferentially associate with mineral species dispersed within the organic matter of the clean coal samples (Taggart et al., 2016).

Ash particle formation in a pulverized fuel boiler is a complex process that is controlled by multiple factors –mineral characteristics of the feed, grind size, combustion conditions, and the direction and velocity of the flue gas (Benson et al., 1993). Ash formation during pulverized coal combustion is described by Seames (2013) and Kutchko and Kim (2006). Studies on the mobility of elements during coal combustion have shown that REE may be homogeneously distributed as micron to nanometer-sized particles in amorphous aluminosilicate glass, also referred to as slag (Hower et al., 2013; Kolker et al., 2017; Mardon and Hower, 2004; Thompson et al., 2018). Rhabdophane, monazite and xenotime (REE-PO_4) were observed as individual crystals in CUB fly ash matrix or encapsulated by aluminosilicate glass (Thompson et al., 2018). Mardon and Hower (2004) and Hower et al. (1999) demonstrated the impact that source coal properties and combustion techniques, such as temperature, blend, and ash collection points, have on the quality and composition of the combustion byproducts and associated REE. Hower et al. (2013) demonstrate that vaporization, condensation, and crystallization of carbonatite minerals in Ca-bearing igneous rocks is analogous to the formation of solid inorganic mineral particles (e.g., ash particles) during coal combustion and subsequent collection in the bag house.

The objective of this work is to characterize CUB samples that are representative of byproducts produced during the utilization of coal in power generation systems. Pulverized roof rock or reject, produced ash, and disposed materials from coal utilization all provide opportunities for REE recovery. Detailed elemental and mineral phase data are combined with multimodal microanalytical imaging and image processing techniques to classify the two- and three-dimensional morphological, elemental, and mineralogical properties of six CUB samples: three fly ash, one bottom ash, one roof rock, and one pulverized coal reject. This characterization work aids in the discovery of targeted, efficient extraction techniques that bring REY resources into the market in the safest and most economically viable way.

2. Materials and methods

2.1. Materials and elemental analysis

Six representative samples of CUB were selected from the National Energy Technology Laboratory (NETL) coal and coal byproduct field samples database housed on the Energy Data Exchange (National Energy Technology Laboratory Energy Data Exchange (NETL-EDX), 2018). A detailed description of each sample is provided in Table 1 and photographs of the samples are shown in Fig. 1. Major, minor, and trace element concentrations were measured for dried samples by Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) and Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). Detailed methods for the measurement of REE and other trace elements in geologic samples by ICP-OES/MS are discussed in Bank et al. (2016). Ratios of heavy, medium, and light REY are calculated based on the geochemical classification by Seredin and Dai (2012), which divides lanthanides and yittrium (REY) into LREY (La, Ce, Nd, Sm), MREY (Eu, Gd, Tb, Dy, Y), and HREY (Ho, Er, Tm, Lu).

2.2. Microanalysis sample preparation

Fifty grams of each as-received sample (see Fig. 1) was oven dried at 55 °C for 8 h and stored in a nitrogen-purged desiccator prior to analysis. Each dried sample was mixed thoroughly, and subsamples were taken for grain size analysis, X-ray diffraction (XRD) analysis, and SEM analysis. Rock and ash samples for XRD were ground to a uniform powder that passed through a $< 63\,\mu m$ (230-mesh) sieve. Samples for electron imaging and microanalysis were mounted as powder grain mounts on 1-cm diameter metal stubs backed with conductive carbon tape, or mounted in epoxy and polished.

2.3. X-ray diffraction

Bulk mineralogy of rock and ash samples was determined by X-ray diffraction (XRD) of a randomly-oriented powder mount. Powdered samples were mounted in cavity mounts on an automatic sample changer with a spinner. XRD patterns were collected using a PANalytical X'Pert Pro diffractometer equipped with copper radiation and an X'Celerator parallel plate detector. The samples were scanned at 45 kV, 40 mA over a range of 4.0–70° two-theta in continuous mode with a step size of 0.033° and a count time of 1000 s. Phase IDs, peak alignments, and mineral identifications were made via comparison of the diffraction peaks against the PDF4 + - ICDD database (ICDD, 2016) in PANalytical HighScore Plus. Semi-quantitative analysis of the